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(73) Holder of patent:
Hagedorn AG, 49078 Osnabrück, Germany

(74) Agent:
Busse & Busse Patent Attorneys,
49084 Osnabrück

(54) Plasticized Cellulose Nitrate

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Plasticized Cellulose Nitrate

The invention relates to plasticized cellulose nitrate consisting of cellulose nitrates having a nitrogen content of 12.6 % by weight or less. It is known how to employ plasticized cellulose in the production of paints and varnishes, finding application particularly in the production of leather varnishes and furniture varnishes. Additionally, it is used in the production of adhesives and printing ink, in particular for rotogravure (or plate) printing for packaging, flex-printing and screen printing. Through the use of softening agent/cellulose nitrate mixtures the bonding strength, application in reactive systems (e.g. Diisocyanates) and the processing properties of these products are essentially improved.

Here phthalate-containing softeners as, for example, dioctylphthalate (DOP/DEHP) or dibutylphthalate (DBP) are chiefly added to the cellulose nitrate mixture. However, from the point of view of environmental compatibility and health hazards, these substances display considerable disadvantages. Thus, dioctylphthalate or dibutylphthalate can possibly impair reproduction capability, as well as provoke damages to the unborn child in the mother's womb. Moreover, dibutylphthalate can cause long term damaging effects in waters.

Therefore it is known from EP 0 472 076 A1 how to use epoxidized soy bean or linseed oil as a substitute substance for phthalate-containing softeners. These substances, on the one hand, distinguish themselves in that they are neither hazardous to health nor damaging to the environment, on the other hand, however, they are not optimally compatible with cellulose nitrate.

The task of the invention is to obtain a plasticized cellulose nitrate that is characterized by a low risk to health and a high environmental compatibility, with the softener components being very compatible with the cellulose nitrate, and, along with lower solvent retention, being resistant against migration.

It was found that this objective can be achieved with a mixture of cellulose nitrate having a nitrogen content of less than 12.6% by weight and esters of adipic acid

and/or citric acid and/or sebacic acid and/or esters of sugars and/or polyols with various acids and/or colophony (rosin) derivatives, as phthalate-free softeners or soft resins.

For producing cellulose nitrate/softener mixtures in accordance with the invention, commercial cellulose nitrates of different viscosity grades with a nitrogen content of 10-12.6% by weight are preferably utilized. Preferred mixtures are those that consist of 82-40% by weight, preferably 82-75% by weight, of cellulose nitrate and 18-60 % by weight, preferably 18-25% by weight, of esters of adipic acid and/or citric acid and/or sebacic and/or esters of sugar and/or polyols with various acids and/or colophony (rosin) derivatives. Preferably suited here are the following esters:

- Dibutylsebacetate (DBS)
- Diisobutyladipate (DIBA)
- Diocytladipate (Di-2-ethyl-hexyladipate/DOA).
- Succeroseacetoisobutyrate (SAIB),
- Methyldihydroabietate (Hercolyn D),
- Acetyltributylcitrate (ATBC), or
- Polyesterpolyol Rokraphen 145.

As end product, the plasticized cellulose nitrate is present in the form of hard, colorless, irregularly broken platelets, which are also described as colorless chips.

The properties of the phthalate-free or soft resins in cellulose nitrate will be explained in still more detail in the following, in comparison with customary types of softeners.

The known phthalate-containing softeners such as dioctylphthalate (DBP) and dibutylphthalate (DOP), as well as epoxidized soy bean or linseed oil on the one hand, and the phthalate-free softeners in accordance with the invention dibutylsebacetate (DBS), diisobutyladipate (DIBA), dioctyladipate (DOA), triethylcitrate (TEC), acetylbutylcitrate (ATBC), as well as the soft resins succeroseacetoisobutyrate (SAIB), methyldihydroabietate (Hercolyn D) and

polyesterpolyol Rokraphen 145 on the other hand, were investigated relative to their resistance to cold, their light resistance against turning yellow, their gelatinizing behavior, their resistance to heat, their ductility, their resistance to buckling, their luster behavior, their reactive capability, resistance to migration and solvent retention. The results of these investigations are laid out in table 1.

The investigations showed that the phthalate-free types of softeners in accordance with the invention are superior in every point, relative to the properties investigated, to the phthalate-free epoxidized soy oils known up until now. However, at least comparable if not even better results are also to be achieved with softener types in cellulose nitrate mixtures in accordance with the invention, in comparison to the known phthalate-containing softeners DBP and DOP.

Fron this it follows that, solely on the basis of the physical qualities investigated, the softener types in accordance with the invention display considerable advantages compared to the currently known types of softeners.

Furthermore, the phthalate-free softeners or soft resins in accordance with the invention distinguish themselves by good compatibility with the cellulose nitrate, a low environmental hazard, as well as a low health risk. Moreover, the soft resins distinguish themselves by low solvent retention and good resistance to migration. Further presented in Table 1 as a measure for assessment are both the identification of the Hazardous Substances Regulation in Germany as well as the approval of the "Food and Drug Administration" in the USA for coating of foodstuffs packaging.

Claims

1. Plasticized cellulose nitrate consisting of cellulose nitrate having a nitrogen content of 12.6% by weight or less and phthalate-free softeners, characterized by the fact that provided as phthalate-free softeners are esters of adipic acid and/or citric acid and/or sebacic acid and/or esters of sugars and/or polyols with various acids and/or colophony (rosin) derivatives.

2. Plasticized cellulose nitrate according to Claim 1, characterized by the fact that it consists of commercial type cellulose nitrate of different viscosity grades having a nitrogen content of 10-12.6% by weight.

3. Plasticized cellulose nitrate according to Claim 1 or 2, characterized by the fact that it consists of 82-40% by weight of cellulose nitrate and 18-60% by weight of ester of adipic acid and/or citric acid and/or sebacic acid and/or esters of sugars and/or polyols with various acids and/or colophony (resin) derivatives.

4. Plasticized cellulose nitrate according to Claim 1 or 2, characterized by the fact that it consists of 82-75% by weight of cellulose nitrate and 18-25% by weight esters of adipic acid and/or citric acid and/or sebacic acid and/or esters of sugars and/or polyols with various acids and/or colophony (rosin) derivatives.

Table 1
Comparison of various types of softeners in cellulose nitrate mixtures

	DBP	DOP	DINP	Epox. Soy oil	DBS	DIBA	DOA	TEC (Citro-flex 2)	ATBC (Citroflex A4)	SAIB	Rokraphen 145	Hercolyn D
FDA approval per § 175.300	No	Still in Process	No	Yes	Yes	Yes	Yes	Yes	Yes	No §175.105 yes	Yes	Yes
Heat resistance	Good	Good	Good	Low	Very good	Very good	Very good	Good	Good	Good	Good to very good	Low
Light resistance against yellowing	Good	Good	Good	Good	Good	Very good	Very good	Very good	Good	Very good	Good	Almost good
Gelatinizing behav-ior (antisweating behavior	Good	Almost good	Almost good	Low	Very good	Very good	Good	Very good	Very good	Very good	Very good	Very good
Heat resistance	Almost good	Good	Good	Very good	Good	Almost good	Good	Almost good	Good	Very good	Very good	Very good
Ductility	Good	Almost good	Almost good	Low	Very good	Very good	Very good	Good	Very good	Low	Almost good	Low
Resistance to buckling	Good	Almost good	Almost good	Good	Very good	Very good	Good	Good	Very good	Low	Good	Low
Luster behavior	Very good	Good	Good	Almost good	Very good	Very good	Very good	Very good	Good	Very good	Very good	Very good
Reactive (free OH groups or epoxy groups)	No	No	No	Yes (epoxy)	No	No	No	Yes (OH)	No	No	Yes (OH)	n.a.
Migration resistance	No	No	No	No	No	No	No	No	No	Yes	Yes	Yes
Solvent retention	Low	Low	Low	Low	Low	Low	Low	Low	Low	Some	Hardly	Perceive-able
Designation based on hazardous sub-stances regulation												
Environmentally hazardous	Yes	No	No	No	No	No	No	No	No	No	No	No
Damaging to health	Yes	Yes	No	No	No	No	No	No	No	No	No	No